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OVERVIEW OF THERMOCHEMICAL CONVERSION BIOMASS IN CANADA

PREPARED BY:

R.D. Hayes
Chief, Bioenergy Research and Development
Technology Branch
Energy, Mines and Resources Canada
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SUMMARY

Thermochemical conversion of biomass in Canada has undergone a considerable transformation in approach and expectations over the last ten years. A decade ago, the promise of early commercialization quickly evaporated and was replaced by a more realistic assessment that the potential would likely not materialize except over the longer term. More recently, this outlook has been modified slightly in the wake of unanticipated research progress and the surfacing of some special near-term market applications.

RÉSUMÉ

Depuis dix ans, la conversion thermodynamique de la biomasse au Canada a évolué considérablement, tant sur le plan de l'approche que sur le plan de ce qu'on comptait en tirer. Il y a dix ans, on a vu s'évanouir l'espoir d'une commercialisation rapide et on a plutôt adopté l'attitude plus réaliste que cette technologie ne pourrait atteindre son plein potentiel qu'à long terme. Plus récemment, cette perspective s'est modifiée quelque peu à la lumière de résultats imprévisibles de recherche et de l'émergence sur le marché de nouvelles applications réalisables à court terme.

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R.D. HAYES
Bioenergy Research and Development
Technology Branch
Energy, Mines and Resources Canada
Ottawa, Canada K1A 0E4

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1. INTRODUCTION AND HISTORY

During the late 1970's and early 80's there was a short-lived perception of panic in energy security accompanied by exaggerated claims of technical readiness of thermochemical conversion applications. Several premature commercial demonstrations in the U.S.A. of pyrolysis and gasification failed technically and financially. Governments and investors became understandably cautious therefore when further approached by technology vendors. American communities that once considered gasification and pyrolysis of municipal solid wastes as environmentally attractive alternatives to relieve pressure on decreased availability of landfill sites for urban refuse, turned their attention to mass incineration and refuse derived fuel (RDF) combustion applications. Though environmentally less attractive in terms of emissions, combustion offered less technical and financial risk than did the more exotic thermochemical conversion options.

Canada was somewhat behind the U.S.A., having felt less apparent impact from the energy supply disruptions of 1973 and 1979. In those days also there was less pressure to find alternatives to landfilling of wastes than there was in many U.S. cities, or, as there is in some Canadian cities today. Canadian thermochemical conversion research, then in its infancy, therefore focussed its effort on the long term. It assumed a lengthy timeframe to mature innovative process developments. In theory, this new breed of technologies would presumably become technically ready for the 1990's or 21st century, in a world eager to embrace bioenergy, particularly from wood, as a sustainable and environmentally attractive energy resource.

The ultimate vision of some researchers was to refine biomass in a manner analogous to petroleum that would eventually lead to alternative transportation fuels, preferably high quality gasoline, plus a host of high value byproduct specialty chemicals. As the bubble burst on high world oil prices, the sense of urgency to accelerate R&D diminished. Admittedly, severe federal budget reductions for energy R&D also had its predictable effect on the "sense of urgency". Except for one major project, gasification research in Canada all but disappeared by 1984. The pyrolysis/liquefaction research community collectively agreed to back off from upgrading studies, and concentrated instead on perfecting their processes for primary oil production.

Over the past decade, the science has become better understood and technical advances have actually surpassed earlier expectations. Some laboratories have begun to re-activate their upgrading research. Scientists and engineers have broadened the scope of experimental conditions and gained a much deeper understanding of the chemical transformations of complex feedstocks to multiple products.

A new vision of conversion and product opportunities has begun to reshape our view of the timeframe for commercialization. The long term perspective remains paramount, and perhaps even more so since the global call for environmentally sustainable economic development by the Brundtland Commission report, "Our Common Future"[i].

In addition to the long-term vision, technical progress in the identification of several high valued specialty chemicals in wood pyrolysis oil may be the market hook (albeit a small market) required to help finance the high costs of staged scale-up from laboratory, process development unit, pilot plant, small commercial demonstration and eventually to full-scale commercial reality.

Several other near term opportunities have also surfaced. Environmental pressures have influenced the trial experimentation of biomass pyrolysis liquefaction technologies on non-woody feedstocks such as used tires, petroleum sludges, sewage sludge, and, once again, municipal solid wastes. Impending environmental regulatory controls on waste incineration and increasing costs for landfilling may create a climate more ideal for fully contained emission-free thermochemical processes.

Researchers, industry and government have all become more creative in building a diversified, yet comprehensive, portfolio of thermochemical conversion opportunities for the commercial world. Though nothing thoroughly new has emerged, the past ten years have seen an evolution from a subject of technical curiosity to one of concerted effort toward cost effective products for the marketplace, some sooner than others.

2. PROSPECTIVE APPLICATIONS OF TECHNOLOGY (PAT)

A broader diversified portfolio, as referred to above, presents a major challenge to the R&D planner. Added to this challenge is the ever- present restraints in government R&D funding. This challenge has necessitated a major overhaul in organizing R&D priorities in the context of assessing a balance in both near and long term commercialization and environmental opportunities and needs.

The commercialization process for a new technology as defined within the Energy Diversity Division of Energy Mines & Resources Canada includes everything germane including opportunity identification, the actual research, development, technical evaluation, and demonstration as well as the determination of current and projected economic feasibilities, current and future market, expected timeframes for commercialization, standards development, and many other factors affecting market introduction and penetration. Once these elements have been assessed and analyzed for the various feedstock/conversion technology pathways, priorities could be estab-lished with respect to activities that government can, should, or must, do and those that government should not, or cannot afford, to support.

The first step in the process is to organize the four basic elements of a technology by resource (eg. biomass, wastes, peat etc.), process(es), product(s), and market application. The particular feedstock combined with specific conversion processes and a particular market application of products result in what we define as a **Prospective Application of Technology or PAT.** The picture can become rather complex especially when considering combinations of thermochemical, biochemical and fractionation technologies that might be otherwise overlooked during conventional analysis. In order to illustrate many of the various combinations pictorially, we have constructed a **'PAT map.'**

Figure 1 is a simplified version of a **'PAT map'** for thermochemical technologies. One can visualize perhaps one hundred or more probable combinations of resources, processes, products, and market applications. The product possibilities alone include a vast array of oils, gases, chars, carbon black, sugars, fermentation products, high value specialty chemicals, medium value commodity chemicals, olefins, gasoline and gasoline components, diesel fuel, and other materials. Figure 2 is a more general PAT map encompasing most bioenergy technologies.

FIGURE I

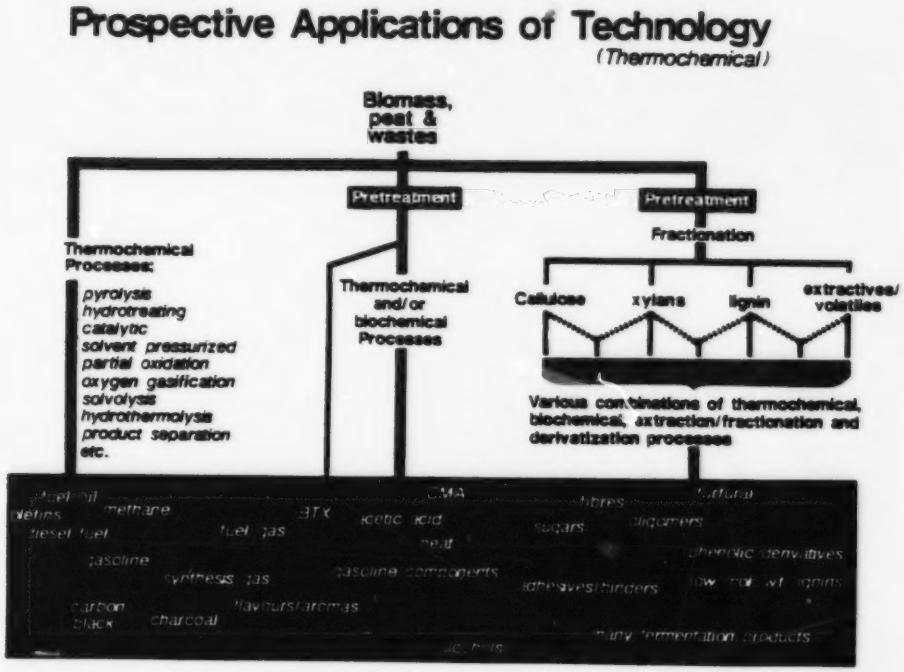
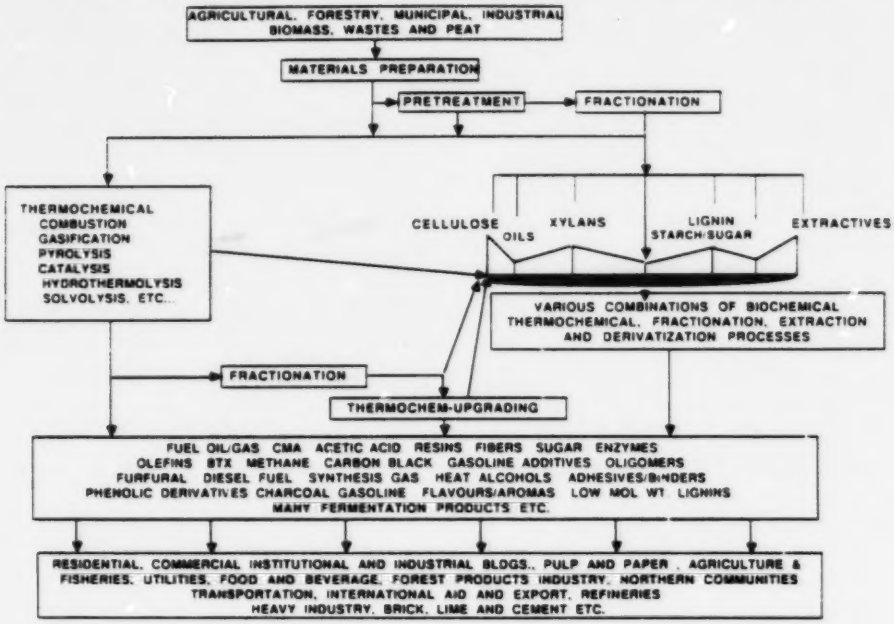


FIGURE II

PROSPECTIVE APPLICATIONS OF TECHNOLOGY



Our view of the world of thermochemical conversion of biomass is no longer limited to merely the pyrolysis or gasification of wood to heating oil and gas. Thermochemical conversion is not treated in isolation from biochemical, fractionation or derivatization processes. Even considering a single process technology, the variation in process conditions, catalysts, reactants, or feedstocks can impact the range and output of possible product combinations.

The second step will be to select a handful of promising PAT's, and perform an analysis of expected technical progress, economic feasibility, market penetration, and timeframe for commercialization. In theory, this should provide government (and industry) with a rationale for desirable government (and industry) activities in those PAT's such as research, development, demonstration, detailed engineering, market studies, economic and financial analysis, information dissemination, standards formulation, etc.

Some of the so-called 'thermochemical PAT's' that are not typically represented at thermochemical conversion of biomass conferences, but which are included or planned for in Energy, Mines and Resources' Bioenergy R&D program planning include the following:

- thermochemical treatment of plant oils (oilseed, tall oil) to produce high cetane diesel fuel.
- biochemical and thermochemical derived lignin that is thermally or thermochemically treated with or without catalysts to produce gasoline and other chemicals.

- product derivation of thermochemical and biochemical lignins (eg. resins, adhesives, cement dispersants).
- thermochemical treatment of the steam fractionated cellulose component of biomass.
- direct steam (thermal) production of adhesives with a fibre byproduct suitable for molding, pelletizing, or thermochemical or biochemical processing.
- calcium magnesium acetate (CMA) production as a road de-icer from aqueous effluents (ie. dilute acetic acid) of pyrolysis and biochemical processes.
- investigation of wheat chaff as a thermo- or biochemical conversion feedstock.
- methanation of pyrolysis aqueous effluents.
- separation of short and long fibers of hardwoods where pulp would be processed from the long fibers and fuels processed biochemically or thermochemically from the lower value short fibers.
- source separated and/or prescreened, or raw, municipal wastes that undergo thermochemical or biochemical conversion with or without pretreatment/fractionation.

3. EMR's BIOENERGY DEVELOPMENT PROGRAM

Table 1 shows the historical trend in Canadian federal government spending on bioenergy R&D including biomass production and conversion. Table 2 is a breakdown of thermochemical R&D expenditures relative to other conversion technology areas.

3.1 BRIEF REVIEW OF NON-THERMOCHEMICAL R&D

The following is a cursory view of Canadian R&D activities in technical areas other than thermochemical.

The **combustion** area's main focus of effort is the evaluation and improvement of industrial and residential combustor performance and emissions. Also included has been support to Environment Canada's National Incinerator Test and Evaluation Program (NITEP) and the development of standards for performance, safety and emissions of residential wood burning appliances.

The **biomass handling/preparation** area includes research in biomass materials handling, storage, drying, beneficiation, and preparation. This research is seen to provide necessary infrastructural support for all biomass conversion processes, but more importantly, to improve biomass fuel quality with objectives to improve biomass combustion performance and to reduce emissions. Examples of developments include a bin, silo and non-consolidating feeder system that regulates the controlled and non-disrupted feeding of hog fuel and chips to burners, a device to exclude frozen lumps of hog fuel and chips to burners, a continuous moisture sensor to provide improved combustion control of biomass of varying water content, and a low energy grinder to powder wood suitable for suspension-fired boilers.

The biochemical area receives the largest allocation of funds, in part due to increasing industrial leverage provided by cost-shared R&D. Much of the impetus for this area comes from mid-term (1990's) competitive potential to enter the transportation fuel

TABLE I

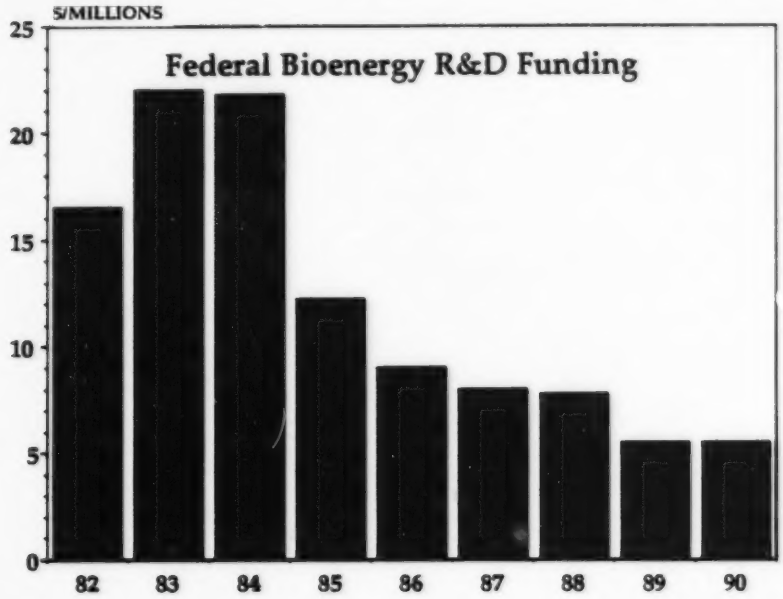
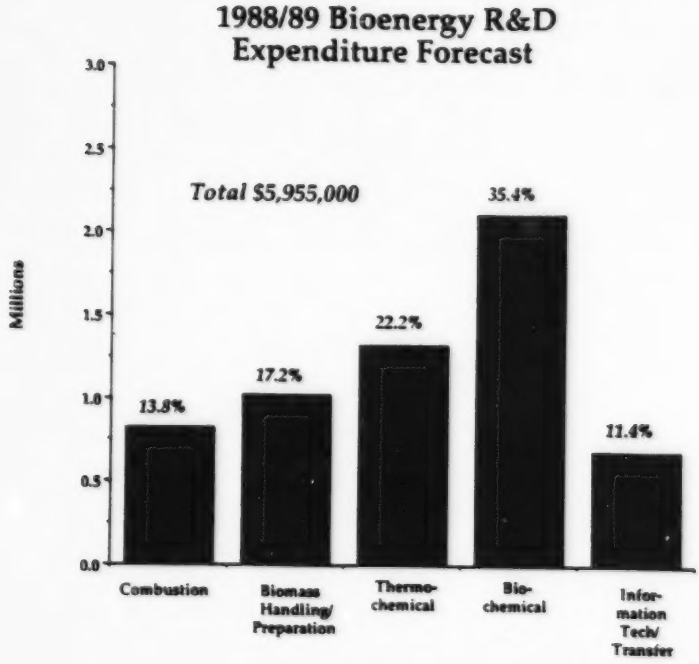


TABLE II



market with biomass derived ethanol based blends and oxygenates and the longer term potential of neat ethanol fuel along with value added byproducts. The program is divided into a number of areas including enzymatic and acid hydrolysis of lignocellulosics, steam and extrusion pretreatment and biomass fractionation, novel fermentation engineering, biotechnology of enzymes and microorganisms, anaerobic digestion, characterization and derivatization of lignin, and the development of non-ethanol byproduct streams, among others. The rate of achievements in this area over the past four years rivals that in the thermochemical area. The lure and promise of biotechnology and the recent accelerated progress are likely the major factors in attracting industry participation in an area that was viewed by our program as very long term as of only five or six years ago.

3.2 CANADA'S MAINSTREAM BIOMASS THERMOCHEMICAL CONVERSION R&D

An approach has evolved in Canada whereby, unlike earlier efforts, a whole range of products and reactants are now considered. Products include gases and oils of varying quality, sugar solutions in high yield, chemicals (olefins, phenolics, as well as high value specialty chemicals), gasoline or diesel fuel, and higher value carbon products. Diversification of reactants include whole biomass, fractionated biomass components, peat, and muncipal solid waste, including source-separated wastes such as used tires. Another area of research is the treatment, and especially, the conversion, of waste aqueous effluents from thermochemical conversions into value-added co-products. Left unprocessed, these effluents would otherwise incur a cost for waste treatment.

3.2.1 GASIFICATION

Canadian developments in biomass gasification for the production of low, medium and high energy gases have enjoyed world technical acclaim over the past decade, but there has been a disappointing uptake by Canadian industry. The cautious attitude of our industry appears to have been due largely to premature and unsuccessful attempts in the US to commercialize immature technologies during the latter '70s and early '80s. A possible revival of interest in gasification technology applications appears to be for replacing industrial boilers that use oil and for municipal energy from waste projects. The work to complete ongoing projects will continue, although at a reduced level, and any impetus for an expanded government program will likely wait for stronger industry confidence, interest, and cost share. Application of Canadian technology in developing countries may hold some promise.

Large scale (10 tonnes/hour) gasification technology, developed through the Biosyn project offers a world leading technology in pressurized, air or oxygen fed, fluidized-bed gasification that can be adapted to the production of synthesis gas for methanol production or low energy gas for other applications such as space heating, gas turbines or industrial diesel engine operation.

Another portion of the gasification research funds is directed to the development of a small scale gasifier that is designed to use wet wood and produce a clean gas. The Heuristic gasifier is a two-stage reactor that, in principle, operates similarly to a downdraft design. The first stage is an updraft gasifier where producer gas and condensible vapours (tars)

are routed through a hot char bed below. The tars are to be cracked in the second stage. The project now underway is to modify the gasifier, optimize the operating parameters, and enhance cracking in the second stage.

3.2.2 LIQUEFACTION/PYROLYSIS

In 1985, research in the direct liquefaction of biomass was expected to wind down because the rapid commercialization that was expected to occur in the early '80s did not materialize. The plan was to conclude as much of the work as possible, revert to lower cost basic research, and pursue a strategy of chemicals from liquefaction. Then in 1986 there appeared to be a turnaround in commercial interest. Unprecedented technical achievements started to renew aspirations and industry interest in exploiting selected market niches for pyrolysis products. The following is a brief review of current projects.

McGill University

Over the past several years researchers W.J.M. Douglas and D.G. Cooper at McGill University have been studying an interesting thermochemical approach to wood liquefaction using aqueous hydrogen iodide at fairly mild conditions of pressure and temperature (125°C). Still far from certain is the exact nature of the liquid products and the techno-economic practicality of hydrogen iodide recovery and recycle. On the positive side, in addition to the low severity conditions of reaction, the process removes about 80% of the oxygen in the wood, and the char yield is low.

University of Toronto

D.G.B. Boocock and co-workers at the University of Toronto have undertaken the investigation of steam pyrolysis or hydrothermolysis of wood. Based on their earlier work, they recently designed and constructed a laboratory scale cascade autoclave which can accommodate up to 100 g of wood chips or 170 g of a single larger piece (3.8 cm reactor I.D., 600ml volume). It is rated at 24.1 MPa (3500 psi.) at 350°C allowing for 7.6 MPa (1100 psi) gas overpressure above the vapour pressure of water at that temperature. Replicated results indicate that oil yield increases with increased chip size. Dry product oil yields are high (up to 50%) with no solids contamination, and the oil is easily separable from the aqueous phase. Coupled with an upgrading process, this technology may someday lend itself well to commercialization.

In addition to their process development work, Professor Boocock's group has contributed greatly to the basic understanding of biomass liquefaction, especially through their scanning electron microscopic studies. The group at the University of Toronto is also performing upgrading studies through the catalytic hydrotreatment of model compounds. Of potential interest too is their discovery in 1984 that a particular clone of hybrid poplar yielded 6% phenol. This discovery raises the prospect of matching processes more closely with specific feedstocks in the interest of optimizing a particular product slate. Efforts are now beginning to genetically engineer trees that are designed for specific process/product applications.

Université de Sherbrooke

E. Chornet, R.P. Overend and co-workers at the Université de Sherbrooke have been working on a liquefaction process in pressurized solvent for some years. Their approach involves an overall integration of biomass pretreatment, fractionation, acid processing, thermochemical and biochemical treatment.

Funding for research at Sherbrooke in the areas of peat and wood conversion is provided by a number of sources, including Energy, Mines & Resources. The program there involves a comprehensive variety of fundamental studies, product engineering and technology development at laboratory and pilot plant levels. Examples of approaches under investigation include a thermo-mechanical-chemical treatment to fractionate and liquefy biomass including steam treatment, thermocatalytic conversion of fractionated products such as lignin to monomers, ethylene glycol solvolysis/liquefaction, acid/thermal/shear treatment of biomass and cellulose, and a variety of biochemical investigations in combination with thermochemical techniques. In association with other laboratories, the chemical engineering laboratory of Professor Chornet is especially well equipped for analytical characterization of products derived from their various reaction systems.

University of Waterloo

D.S. Scott, J. Piskorz, D. Radlein and co-workers at the University of Waterloo are well known for their fluidized bed flash pyrolysis development, also known as the WFPP (Waterloo Fast Pyrolysis Process). A number of companies and the European Economic Community have indicated their interest in collaborating with the Waterloo group. The WFPP actually includes five process options as follows:

1. Direct thermal processing at 450-550°C, atmospheric pressure, and about 500 ms vapour residence time. They report high liquid yield (80% including water, based on input wood) that is a suitable fuel for conventional boilers.

2. By varying the process conditions and adopting a mild sulphuric acid pretreatment of wood followed by fluidized bed thermopyrolysis, the WFPP produces a high yield and concentration of anhydro-sugars rather than oil products. Their reproducible yields of sugars from pure cellulose are about 80% of theoretical in a concentrated form. One can easily speculate whether this development could challenge some of the equally exciting biochemical conversion methods of converting lignocellulosics to fermentable sugars.

3. Waterloo's hydrogasification work has been technically highly successful, resulting in 75% conversion of wood carbon to methane via pyrolysis over a nickel-alumina catalyst with hydrogen at about 550°C and 440 ms vapour residence time.

4. Under current investigation is a fourth process option of producing polyolefins from wood in a catalyzed reaction. Apart from the use of catalysts, the process equipment and operating conditions are very similar for all of the above process options.

5. The Waterloo group is also performing upgrading research by catalyticly hydrotreating pyrolysis oil fractions, especially lignin, in a continuous pressurized reactor.

University of Western Ontario

Although not currently funded by Energy, Mines & Resources, M. Bergougnou, R. Graham and co-workers have developed an Ultra-Rapid Pyrolysis or Ultrapyrolysis process at the University of Western Ontario. Although there are similarities in this work and the research at the University of Waterloo, there are important differences. Whereas the Waterloo process utilizes fluidized-bed heat transfer, Professor Bergougnou employees a very rapid (30ms) mixing and heat transfer in a vortical contactor or vortactor followed by a plug-flow entrained-bed down flow reactor (50-900ms) and quenching (30ms) with cryogenic nitrogen in a cryovortactor. Dissimilar to the Waterloo process are the process conditions (650-1000°C, 50-900 ms residence time), and the main product at these temperatures is gas rather than liquid. Since pyrolytic fuel gas production has not been of high priority in Canada's bioenergy R&D strategy, the current objective, in collaboration with Ensyn Engineering, (see below) is the production of chemicals and, in particular olefins.

It is interesting to note here that the Universities of Waterloo and Western Ontario conducted an extensive data comparison from each of their reactor systems. Using selected data from both groups at around 500 ms residence time, liquid and gas production data were plotted vs temperature. The temperature ranges were as follows: Waterloo at 400°-750°C, and Western Ontario at 650°-900°C. With combined data for each of the gas yield vs temperature and liquid yield vs temperature respectively there was remarkable agreement of data in overlapping regions. A simple first order kinetic model is able to describe the oil yield over the temperature range of both experiments.

Ensyn Engineering

Ensyn Engineering is a recently formed company whose principal investigator, R. Graham has scaled up the University of Western Ontario Ultrapyrolysis reactor by a factor of 20 to a 5-10 kg/hr capacity RTP (Rapid Thermal Processor). The reactor is designed to accept any carbonaceous feed (solid, liquid, or gas) by injecting it into a turbulent cloud of hot solids. The mixed feed plus solids is carried through a tubular transport reactor to an inertial separator where vapour products are removed. This project is co-sponsored by the private sector.

Work planned for 1989 involves thermal cracking and catalytic treatment of pyrolysis oils and various lignin preparations including steam exploded biomass derived lignin.

Laval University

Multi-stage vacuum pyrolysis was developed by C. Roy and co-workers, initially at the Université de Sherbrooke and, currently, at the Université Laval. The technology consists of a 40 kg/hr multiple hearth vacuum pyrolysis process development unit located near the Université Laval. There is also an industrial cost-shared pilot demonstration of a

single-stage process at St-Amable, Quebec. The unit has a capacity of 200 kg/hr and is designed for used tires.

Although the multiple hearth concept suffers from low heat transfer relative to other pyrolysis processes, and, at first glance, is capital cost intensive, it has a number of redeeming features that show commercial promise as follows:

1. A high yield of pyrolysis oil (50% based on wood).
2. The production of co-product carboxylic acids and high value chemicals.
3. Reactive charcoal at 25% of input wood.
4. The aqueous phase is recovered separately as vapour or liquid as an integral part of the process leaving a low water content water-free pyrolysis oil ready for upgrading.
5. The multiple hearth performs a product fractionation function that could reduce extraction costs of high value chemicals.

Centralized Analysis

One final work of interest in Canada is a Centralized Analysis project at B.C. Research. In 1984, a trial project was set-up whereby different Canadian bio-oils could be compared in a standard manner. The project embraced a three-pronged approach. Under the guidance of J. Howard and J. McKinley, B.C. Research performed and/or coordinated the centralized analyses of optimized oils produced by each researcher. Individual researchers also did some of their own analyses to obtain immediate experimental feedback.

The second prong of the approach was that all researchers were provided with a standard wood sample, Populus deltoides, by Forintek Canada Corp. The idea was that when each process development became somewhat optimized, the researcher would submit oil from the standard wood sample to the centralized analysis team.

The third prong was a computer communications network link called CoSy, through the University of Guelph, to provide fast communication of analytical data. It was also used to encourage multilateral and bilateral collaboration and problem solving.

The centralized analysis project has entered Phase II. Learning from the successes and pitfalls of the first two and one half years, the scope of this project has changed somewhat. Phase II has two major tasks.

Task 1 is a set of analytical techniques along the same lines as the initial project except the methods that were considered to be less interesting to the entire group are not included. The basic analyses of task 1 include the following:

- Elemental Analysis
- Water Content
- Density
- Carboxylic Acids
- Gas Liquid Chromatography
- Carbon-13 NMR
- Gel Permeation Chromatography

Task 2 consists largely of special analytical projects to meet the special needs of individual researchers, Energy, Mines and Resources Bioenergy Development Program or groups of thermochemical conversion researchers that may arise over the next two years.

4. INTERNATIONAL VIEW - IEA

Under the International Energy Agency, eleven countries signed a three year Bioenergy Agreement on Cooperative R&D, effective January 1, 1986 to December 31, 1988. This Agreement has since been extended by another three years. Canada, USA, Sweden and Finland agreed to collaborate on a project entitled Direct Biomass Liquefaction (DBL). A Working Group of engineers and other specialists are preparing a detailed technical-economic assessment (TEA) at commercial size scale-up and operation of the most promising high and low pressure pyrolysis/liquefaction processes. Both primary oil production and upgrading are considered in the TEA. The upgrading work on Canadian atmospheric and vacuum pyrolysis oils has been conducted by D. Elliot at Battelle Pacific Northwest Laboratories. Yields of products in the gasoline boiling range have so far reached 35% of primary oil by hydrotreating. The Working Group is attempting two types of analyses, one based on current state of the art and the second based on projected improvements and developments in the technologies.

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The author wishes to acknowledge the various researchers in North America without whose ideas, open discussion, and dedication to research in thermochemical conversion of biomass, this paper would not have been possible. Each has contributed to this paper, either directly or indirectly. The following list is not complete, but includes the principal investigators in Canadian laboratories and other notable international collaborators. In alphabetical order, many thanks to Narendra Bakhshi, Dave Beckman, Dave Boocock, Jean Bouchard, Maurice Bergougnou, Michel Bertrand, Esteban Chornet, Maurice Charron, Helena Chum, Jim Diebold, Allan Dolenko, Murray Douglas, Guy Drouin, Dick Eager, Doug Elliot, Bob Graham, Guy Gravel, Michele Heitz, Ed Hogan, John Howard, Serge Kaliaguine, Bjorn Kjellstrom, Bill Lowe, Tom Milne, Hugh Menard, Jim McKinley, Ralph Overend, Hooshang Pakdel, Jim Pepper, Jan Piskorz, Desmond Radlein, Tom Reed, Joe Robert, Christian Roy, Tom Tidwell, Don Scott, and their many colleagues, staff, and students.

REFERENCES

This paper contains technical contributions including progress reports from all the Canadian and other workers mentioned here. The reader is referred to these individuals or their published papers as primary references.

1. Brundtland, Gro Harlem. 1987 "Our Common Future". World Commission on Environment and Development.